GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[x] ORIGINAL [ ] REVISION NO. ____

Project No. G-33-607# DATE 11/5/81

Project Director: Dr. R. F. Browner School/Lab XXX Chemistry

Sponsor: National Science Foundation; Washington, D. C. 20550

Type Agreement: Grant No. CHE-80-19947

Award Period: From 8/1/81 To 1/31/85* (Performance) ---- (Reports)

Sponsor Amount: $125,000 ($117,873 - Chem + $2,283 - AE + $4,844 - ChE) Contracted through: GTRI ~~GIT~~

Cost Sharing: $3,133 (G-33-372)

Title: Sample Preparation and Introduction for Analytical Atomic Spectroscopy

ADMINISTRATIVE DATA OCA Contact Don S. Hasty x-4820

1) Sponsor Technical Contact: See page 3

Henry N. Blount III
Chemical Analysis Program Director
Division of Chemistry
Directorate for Mathematical & Physics Sciences
National Science Foundation
Washington, D. C. 20550
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2) Sponsor Admin/Contractual Matters: Grants Official *

Paulette L. Green
Section I, MPS/STIA Branch
Division of Grants & Contracts
Directorate for Administration
National Science Foundation
Washington, D. C. 20550
(202) 357-9630

Defense Priority Rating: None Security Classification: None

RESTRICTIONS

See Attached NSF Supplemental Information Sheet for Additional Requirements.

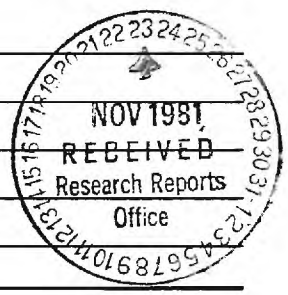
Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT

COMMENTS:

* Includes a 6 month unfunded flexibility period.

\# Subprojects are E-16-640/Powell and E-19-635/Matteson



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FORM OCA 4:781

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

SR519 2-

Date August 9, 1985

Project No. G-33-607 School/~~Lab~~ CHEM

Includes Subproject No.(s) E-16-640/Powell and E-19-635/Matteson

Project Director(s) Dr. R. F. Browner GTRC / GIT

Sponsor National Science Foundation

Title Sample Preparation and Introduction for Analytical Atomic Spectroscopy

Effective Completion Date: 1/31/85 (Performance) 4/30/85 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [ ] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [X] ~~Final Report of Inventions~~ Patent Questionnaire
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other

Continues Project No. Continued by Project No.

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FORM OCA 69.285

Research Proposal Submitted to the National Science Foundation

Technical Report on Grant No. CHE80 19947

"Sample Preparation and Introduction for Analytical Atomic Spectroscopy"

Principal Investigator: Richard F. Browner
Co-Principal Investigator: Michael J. Matteson

Georgia Institute of Technology
School of Chemistry
Atlanta, Georgia 30332

Summary of Accomplishments During Period 8/1/81-3/19/82

1. Fundamental Studies on Aerosol Transport

A number of studies are in progress, relating fundamental properties of the generation and transport of aerosol in atomic spectrometric systems, to the magnitudes of signals and interferences.

(i) Transport Model. A comprehensive model, describing for the first time the interaction of all stages in the transport of liquid aerosol in atomic absorption (AA) and inductively coupled plasma (ICP) systems, has been developed. The model considers the process in three stages. The primary step involves the generation of aerosol, which may be adequately described using the Nukiyama and Tanasawa equation (1). The secondary step applies where an impact bead is placed in the aerosol stream. This may cause both generation of new aerosol and loss of larger aerosol particles. The tertiary steps are predominantly loss processes, as a result of impaction, turbulence, gravitational, and centrifugal processes. Aerosol evaporation can, however, cause an increase in aerosol transport. Mathematical expressions have been developed which give a reasonably good fit between theoretical and experimental data for all these processes.

The very important concepts of useful and excess analyte mass contained in specified drop size ranges have been developed. These show excellent correlation with observed signal magnitudes and interference effects in atomic absorption spectroscopy (e.g. Ca contained in aerosol droplets >4 μm is shown to contribute negligibly to the AA signal; Ca in droplets >2 μm is shown to be very prone to classical phosphate interference).

Finally, the concept of droplet cutoff diameter, being the diameter of the aerosol droplet which corresponds to a 50% reduction in aerosol mass from the peak value on the distribution curve, is introduced. The application of this value, obtained experimentally, to theoretically derived droplet distribution curves, allows prediction of practically important parameters. These include the transport efficiency, ε_n, and the mass of analyte transported to the atom cell per second, W. Correlation between semi-theoretical and experimental values is excellent.

This work will be published shortly as: "Aerosol Transport Model for Atomic Spectrometry", R. F. Browner, A. W. Boorn, D. D. Smith, Anal. Chem. 1982, in press.

(ii) Method for Direct Measurement of Transport Efficiency. Traditional methods for transport efficiency (ε_n) measurements involve indirect procedures. The amount of analyte passing to waste is determined, and subtracted from the amount of analyte aspirated. The procedures we have developed involve direct collection of aerosol either on a filter or on a cascade impactor. The procedure has been tested very thoroughly on a wide range of nebulizer/spraychamber combinations and shown to give typically 5x better precision and up to 4x better accuracy than indirect measurements. This improvement in measurement quality has been crucial in allowing the development of many of the detailed aerosol transport models described in other parts of this report.

This work has been published: "Measurement of Aerosol Transport Efficiency in Atomic Spectrometry", D. D. Smith, R. F. Browner, Anal. Chem. 1982, 54, 533.

(iii) Aerosol Evaporation Properties/Laser Scattering. Our work with laser scattering, for monitoring evaporation and transport properties of aqueous aerosols, continues. The approach using Mie scattering has been tested thoroughly against our well-characterized cascade impactor approach, where possible. Limitations in the Mie scattering approach can give rise to erroneous values for mean droplet size when a large fraction of the aerosol has evaporated to below the lower response limit of the measurement (e.g. <0.2 μm). Nevertheless, the non-intrusive aspect of the approach has led to some very important data on evaporation rates of aerosols as a function of analyte concentration. For aqueous aerosols, evaporation appears to be very rapid, and to take place predominantly as the aerosol is formed. Subsequent evaporation during aerosol transport appears to be quite slow.

A publication describing this work is in preparation: "Mie Scattering for Aqueous Aerosol Characterization", R. Kull, R. F. Browner, 1982.

(iv) Correlation of Analyte Volatility, Droplet Size and Atomic Signal. The development of an "optimum" aerosol for atomic spectrometry requires some knowledge of the behavior of the aerosol in flames and plasmas. Certain, very large, single droplets have been injected into flames and signals observed. However, no correlations have been attempted between droplet size, signal and volatility of analyte for "real" aerosols. By using a range of aerosol types, characterized for droplet size distribution, we have been able to show particle size effects for several elements (Zn, Ca, Al) in both air/C_2H_2 and N_2O/C_2H_2 flames. These curves show that even for volatile elements, such as Zn, there is a direct relationship between particle size and signal.

By choice of an optimum particle size range, the evaporation of particles becomes very efficient. We are now able to specify maximum particle size for optimum atomization for the elements studied.

A publication describing this work is in preparation: "Correlation of Analyte Volatility, Droplet Size and Atomic Signals", D. D. Smith, R. F. Browner, 1982.

2. Sample Introduction Studies

(i) Volatile Metal Chelate Sample Introduction. The earlier studies with preparation and analysis of metal β-diketonate complexes have been continued. The technique has been developed to allow direct and rapid extraction of a number of elements into xylene solvent, which is then nebulized into an inductively coupled argon plasma. This differs from the previous approach, which involved direct volatilization of the β-diketonate complex into the ICP. The solvent extraction approach offers an alternative to the direct vapor introduction procedure, while still giving detection limits in the ng/mL range for Fe, Cn, Zn, Mn, Al and Cr. The trifuloroacetylacetonate complexes of various of these elements have been directly analyzed, with no treatment other than direct reaction, in a sealed ampoule, of the sample with the chelating agent. Good quantitative agreement has been obtained between these procedures and more lengthy acid digestion procedures for human blood serum (Fe, Zn, Cu, Cr), bovine liver (Fe, Cu, Zn, Al, Mn, Cr), orchard leaves (Fe, Cu, Al, Cr) and human skin (Fe).

This work has been published as: "Determination of Metal Chelates by Inductively Coupled Plasma Atomic Emission Spectrometry and Applications to Biological Materials", M. S. Black, M. B. Thomas, R. F. Browner, Anal. Chem. 1981, 53, 2224.

(ii) Organic Solvent Sample Introduction for the ICP. A detailed study has been made of the influence of 30 common organic solvents on ICP emission spectrometry. Correlations have been found between the limiting aspiration rate for the solvent (i.e. the aspiration rate that can be used while sustaining a stable plasma) and the evaporation factor, E, for the solvent. This indicates that solvent vapor loading is the major factor influencing plasma stability with organic solvent introduction.

Signal magnitudes were compared for both aqueous and organic solvents for several elements, and while enhancements were found for the Cu atom line in many solvents, Cr and Fe ion lines were suppressed in volatile solvents. This behavior was attributed to changes in plasma excitation characteristics, caused by solvent vapor interaction with the plasma. Removal of solvent vapor from the aerosol stream by condensation produced signal enhancements of a magnitude consistent with transport efficiency predictions.

The influence of rf power and aspiration rate on solvent tolerance and detection limits was considered and increased power shown to provide some improvements in solvent tolerance. Finally, spectral interferences were studied and shown to be relatively slight.

This work is to be published shortly as: "Effects of Organic Solvents in Inductively Coupled Plasma Atomic Emission Spectrometry", A. W. Boorn and R. F. Browner, Anal. Chem. 1982, in press.

(iii) HPLC Interfacing. The great interest in coupling HPLC and ICP has led us to investigate the properties of the all important interface. Specifically, the positioning of the nebulizer/spray chamber has been shown to be a critical parameter influencing the relationship between peak height and mobile phase flow rate. With a spraychamber placed close

to the end of the chromatography column, peak height becomes largely independent of mobile phase flow rate. In the normal configuration, with a significant length of tubing between column and spraychamber, on the other hand, peak height varies with mobile phase flow rate, making separation conditions more difficult to optimize. The performance of the two configurations is examined in terms of transport efficiency, dilution factor and sensitivity. Less peak broadening and distortion is shown to occur when the sample is transported predominantly as aerosol compared to when it is transported in the liquid state. The low transport efficiency of such systems is still a major limitation to HPLC/ICP coupling.

This work has been published as: "Spray Chamber Placement and Mobile Phase Flow Rate Effects in Liquid Chromatography/Inductively Coupled Plasma Atomic Emission Spectrometry", B. S. Whaley, K. R. Snable, R. F. Browner, Anal. Chem. 1982, 54, 162.

(iv) Matrix Volatilization Interferences in AAS. A common problem with AAS vs. ICPOES is the greater potential for AAS to suffer from volatilization problems with involatile matrix components. However, these interferences are very droplet size dependent, as would be expected. We have been able, by reducing the maximum droplet size of the aerosol reaching the flame, to reduce many of these "classical" condensed phase interferences to negligible levels. Examples are the phosphate interference on Ca, the Ti interference on Al, the V interference on Zn. These can all be effectively eliminated by control of aerosol properties, making AAS once again more competitive (though not in all regards) with ICPOES.

This work is in preparation to be published as: "Condensed Phase Interference Problems in AAS: Droplet Size Dependency", D. D. Smith, R. F. Browner, 1982.

Publications During Current Grant Period

1. "Determination of Metal Chelates by Inductively Coupled Plasma Atomic Emission Spectrometry and Applications to Biological Materials," Marilyn S. Black, Michael B. Thomas and Richard F. Browner, Anal. Chem., 53, 2224 (1981).

2. "Spray Chamber Placement and Mobile Phase Flow Rate Effects in Liquid Chromatography/Inductively Coupled Plasma Atomic Emission Spectrometry," Brenda S. Whaley, Kimberley R. Snable and Richard F. Browner, Anal. Chem., 54, 162 (1982).

3. "Aerosol Transport Model for Atomic Spectrometry," Richard F. Browner, Andrew W. Boorn and David D. Smith, Anal. Chem. 1982, in press.

4. "Effects of Organic Solvents in Inductively Coupled Plasma Atomic Emission Spectrometry," Andrew W. Boorn and Richard F. Browner, Anal. Chem. 1982, in press.

5. "Measurement of Aerosol Transport Efficiency in Atomic Spectrometry," David D. Smith and Richard F. Browner, Anal. Chem 1982.

6. "Fundamental Aspects of Aerosol Generation," Richard F. Browner, in Analysis by Inductively Coupled Plasma Atomic Emission Spectrometry, Ed. P. W. J. M. Boumans, John Wiley, in press.

7. "Applications: Organic Samples," Andrew W. Boorn and Richard F. Browner, in Analysis by Inductively Coupled Plasma Atomic Emission Spectrometry, Ed. P. W. J. M. Boumans, John Wiley, in press.

Summary of Accomplishments During Period 8/1/82 to 4/26/83

1. Fundamental Studies on Aerosol Properties

A major part of our research effort is currently devoted to basic studies of wide ranging relevance to sample introduction for plasmas and flames. These studies draw on and expand the scope of the aerosol transport model discussed in the 1981/82 Annual Report. In addition, the role of water in ICP excitation processes has been considered in relation to its transport process.

2. Influence of Water Vapor and Water Aerosol on Inductively Coupled Plasma (ICP) Signals

While it has been recognized for some time that water can exert a profound influence on plasma excitation characteristics, no attempt has been made to quantify this effect to date. During the course of our studies of aqueous sample introduction to the ICP, it appeared clear that the droplets passing to the plasma with typical systems were similar in size to those used in atomic absorption spectroscopy. One would anticipate that the ICP (typical temperature 6000 to 10,000 K) has more than adequate energy to desolvate and atomize larger particles than a typical flame (temperature 2500 to 3000 K).

In order to investigate this apparent anomoly, we have developed a simple measurement technique which allows us to readily characterize the water vapor and aerosol loading contained in gas streams passing to the plasma. The device consists of a silica gel trap and a 0.5 micron pore size glass fiber filter. With the filter in the stream, liquid aerosol particles are removed and the silica gel collects water vapor with high efficiency. The removal of the filter allows both water aerosol and vapor to reach the silica gel traps. With this simple device the total water loading and also the constituent aerosol and vapor loadings can be readily determined.

A system has been devised which allows varying water aerosol and water vapor loadings to be "T"-d in from different generation systems into one final gas stream passing to the plasma. By controlling the various components of aerosol and vapor in the different streams, it is possible to provide a wide range of water vapor and water aerosol loadings to the plasma. This means that it is possible to quantitatively assess the influence of aerosol and water vapor on the plasma excitation properties. A number of elements of wide ranging excitation properties have been examined.

To date, the following conclusions can be drawn: (1) plasma emission signals are extremely sensitive to water vapor and aerosol loadings. In the case of ionic (hard) lines, the addition of water vapor and water aerosol to the plasma can dramatically reduce the excitation signal. For example, a doubling in water vapor loading can cause a reduction in signal of nearly 100 times. (2) Atomic lines are somewhat less sensitive to addition of water vapor and aerosol to the gas stream. (3) Reduction in vapor vapor and aerosol causes enhancement of ionic lines by typically a factor of 10 times for a two-fold water reduction. (4) Atomic lines, on the other hand, are more sensitive to the influence of water reduction, and a similar reduction of water loading causes atomic line intensity to increase by typically a factor of 30 times.

More detailed studies are underway in order to determine the optimum conditions for water vapor and water aerosol loading in the plasma, with a view to the optimization of this parameter, in order to give best excitation conditions. The final step in this study will involve independent optimization of particle size and analyte loading in the plasma, such that the two variables of water loading and particle size may be controlled independently. This should give rise to significant improvements in detection capability with the inductively coupled plasma.

3. Influence of Surface Tension on Analytical Signals in ICP and AA Spectroscopy

For many years the role of surface tension in atomic spectroscopy has been subject to considerable misinterpretation. During the past year we have made a detailed study of the influence of surface tension on the droplet formation properties of a wide range of organic solvents and of aqueous solvents with added surfactant. The organic solvents have been chosen to provide lower surface tension than aqueous solvents while retaining low volatility properties, in order that evaporation should not be a significant factor in determining the transport properties of the aerosol produced. We have shown in previous studies that volatile solvents transport properties are determined largely by the evaporation characteristics of the solvents.

An examination of the characteristics of the aerosol produced by several commercially available atomic absorption and ICP nebulizers and spray chambers showed that, as expected, the drop size distribution of the aerosol reaching the flame or the plasma is determined primarily by the properties of the spray chamber, rather than the properties of the solvent. As a consequence, drop size distribution for a range of organic solvents differ very little from the drop size distributions of aqueous solutions. Similarly, when both anionic and nonionic surfactants are added to aqueous solutions, no noticeable difference in the drop size distribution of the aerosol reaching the flame or the plasma is noticed.

In the case of organic solvents, with low volatility, there may be some enhancement in the transport efficiency of the solvent, due to reduced surface tension, and the production of an initial aerosol with smaller mean particle size. This would be anticipated to translate into a higher analyte transport efficiency. In order to correlate this change in transport efficiency with analytical signals, it is of course necessary to take into account the influence

of the organic solvent on the temperature and excitation characteristics of the flame or the plasma. In the case of the inductively coupled plasma, organic solvents have been shown (see last year's Annual Report) to have a dramatic negative influence on plasma excitation characteristics.

The effect of surfactants on aerosol production is very interesting. The literature is filled with conflicting reports as to whether surfactants can cause enhancements, reductions or any net effect on signals in atomic spectroscopy. Our studies indicate that surfactants cause no noticeable shift in the drop size distributions of aerosols reaching flame or the plasma. In addition, transport efficiencies do not change significantly either. This indicates that the primary drop size distribution has also not changed significantly, compared to pure aqueous solutions. This is surprising, in that the surface tension of the solution will have been reduced drastically by the addition of surfactants. However, their role in the aerosol production process is clearly insignificant. This may be due to the high speed with which new surfaces form in the droplet formation process, which does not allow the orientation of surfactant molecules to play a major role in influencing surface tension.

Nevertheless, it has been observed that there can be enhancement effects for concentrations of anionic surfactants (e.g. SDS) at concentrations above the critical micelle concentration. This we attribute to an aerosol ionic redistribution (AIR) effect, which we discovered in earlier studies for various species. However, the maximum enhancement of signal due to the AIR effect that we have observed is of the order of 20%. This effect appears to be due to the influence of the surfactant on the surface concentration of metal ions during the droplet formation process. This effect, as we have observed earlier, is heavily drop size related. Consequently, when the drop size distribution is modified by imposing various devices into the aerosol stream, the extent of

the enhancement is changed. For example, the use of a mixer paddle in the aerosol stream, which eliminates most of the larger droplets, causes this enhancement effect to diminish dramatically. Devices such as impact beads, which cause production of additional larger droplets, can in fact cause the magnitude of the AIR effect to increase significantly.

4. Studies with Instability of Small Diameter Liquid Jets

Of fundamental importance to the whole field of aerosol introduction in atomic spectrometry is the ability to generate aerosols of known, controllable, and small particle size. This has not proved possible to date with existing technology. As a consequence, we have made a determined effort to develop systems which would allows us to produce such droplets. Our initial studies involved the development of a device based on the system of Berglund and Liu, which works on the principle of ultrasonic-induced instabilities in a liquid jet. The jet then falls apart into droplets of uniform size. However, the weakness of this system, apart from the need for an ultrasonic transducer, is the limitation on the small size of the particles which may be so produced. The minimum diameter of aerosol that can be produced with such a system is twice the diameter of the jet issuing from the orifice. This means that with a 10 μm orifice, the minimum size of droplets that can be produced is 20 μm, which is too large for our purposes.

We have made, as a consequence, a series of studies of the stability properties of very small diameter liquid jets. We have developed the capability to produce extremely small, highly uniform, circular glass orifices in the range 4 to 20 μm diameter. With appropriate pumping capability this has enabled us to generate very high velocity, very small diameter, stable liquid jets of aqueous and organic solvents. We have found that by incorporation of a suitable gas stream at 90° to the liquid jet it is possible to generate a very uniform

aerosol. Furthermore, the drop size of this aerosol approximates that of the liquid jet. It should be emphasized that this device operates in the absence of ultrasonic transducer induced instabilities, and in fact the production of very small, very uniform aerosols now becomes relatively simple. The characterization of this system and the determination of the relationships between gas-liquid velocities and particle size is currently under way.

We believe this device to be of fundamental importance to all aerosol studies in our program. The device is quite novel, and we know of no other comparable aerosol generation facilities in any other laboratory. This gives us a unique capability for carrying out our present studies.

Sample Introduction Studies

1. Flow Injection Analysis of Microliter Biological Samples into the ICP

The ability to obtain all the normal operating advantages of the ICP, namely, large analytical linear range, freedom from interference, and simultaneous multielement capability, while working with microliter samples, is of great importance in clinical and other areas of trace element analysis. As a consequence, we have been continuing with our studies of flow injection and HPLC sample introduction for the ICP. The primary focus of these studies is the interface between the injection system and the plasma. It is here that significant sample loss occurs, resulting in greatly reduced detection capability. However, we have found that by minimizing dispersion effects in the liquid stream, it is possible to obtain good analytical performance even with the significant losses that occur in the interface.

The system consists of a very low dead volume injection valve, of the HPLC type, coupled to a peristalic pump. The injection valve is then joined, via a very small internal volume tube, to a pneumatic nebulizer/spray chamber. The placing of the nebulizer/spray chamber is critical and must be very close to the injection port. This requires removing the spray chamber/nebulizer from

its normal position in the ICP plasma box. The aerosol from the spray chamber can then pass via a length of Tygon tubing to the plasma torch, with very little loss of analytical performance.

By using such a device, it has proved possible to achieve remarkably good performance in comparison with continuous sample introduction, while operating with relatively small samples. For example, comparison for a number of elements has shown that for a 50 µL injection, detection limit values are only between a factor of 2.5 and 3x poorer than for continuous introduction of several milliliters of sample. Likewise, precision data indicate that relatively little deterioration of precision compared to continuous introduction is found. Typical precisions range from .8 to 2% RSD. The analysis of selected NBS SRMs for a wide range of elements has given very acceptable correlation with the certificate values. With these samples a total sample solution of 150 µL was necessary for 3 replicates.

Further work on the reduction of aerosol loss in the interface between the flow injection system and the ICP is currently in progress. Various devices, involving both ultrasonic nebulization and the liquid jet nebulizer described in the section on Fundamental Studies are currently in progress.

2. Electrothermal Atomizer for Sample Introduction in the ICP

The capability of operating with µL samples with high efficiency can be addressed from a number of directions. One of these is through coupling of an electrothermal atomizer with the ICP. Studies by a number of groups have shown that this technique has high potential, but is fraught with practical problems. We have built such an atomizer for our ICP systems. The atomizer is designed to have a number of novel features which should help us in overcoming some of the transport problems which have been determined to be prevelent with earlier designs of this type of system. We are currently incorporating this system into a modular ICP echelle spectrometer system,which will allow us to do

simultaneous analysis of up to 10 elements. The studies will also involve measurement of plasma properties and the optimization of the sample introduction process by means of a simplex procedure.

3. Removal of Interferences in Flame AAS by Control of Aerosol Drop Size

As a continuation of studies described in last year's Annual Report, we have further extended the work aimed at reduction or removal of vaporization interferences in flame atomic absorption spectroscopy. While this might seem at first glance to be a somewhat dated project, in fact, a number of recent developments in commercial instrumentation have made this a very relevant topic. Current generation atomic absorption spectrometers typically provide for an increase in detection capability by the generation of higher density aerosols, through the use of impact beads. However, our studies have shown that aerosols produced using impact beads have a high proportion of large (>5 μm) droplets. As a consequence, these instruments may give rise to severe vaporization interferences. In fact it appears that in this regard instrumentation has taken a step backwards in recent years. We have examined a number of commercial systems and also designed a system of our own which cuts out large droplets. With our modified spray chamber design, we have been able to effectively eliminate all vaporization interferences from AAS. This contrasts with the performance of current instrumentation, which still suffers from severe vaporization interferences in many sample matrices.

This study has been broadened and brought to completion by the incorporation of data for the nitrous oxide acetylene flame. Here the careful control of the drop size has again been shown to give rise to significant improvements in interference freedom for a number of potential interferring matrix problems.

4. Relationship Between Aerosol Characteristics and Analytical Performance for Various ICP and AAS Nebulizers

In order to check the relevance of some of our fundamental studies to

commercially available systems, we considered it worthwhile to attempt to correlate aerosol characteristics and analytical performance of several commercially available AAS and ICP nebulizers and spraychambers. The drop size distributions produced by these systems, together with their transport efficiencies, have been compared for several elements. The aspects of analytical performance considered were: Detection limits and precision of measurement, together with a few selected interferences known to be problematical.

The atomic absorption nebulizers have shown the following general trends: (1) For volatile elements, those nebulizers producing the highest droplet density, even at the expense of increased proportion of large particles, produced the highest analytical signal. (2) The precision of determinations made with aerosols containing a higher proportion of large droplets is poorer than when these large droplets are eliminated. (3) For involatile elements, there is very little improvement obtained when increased aerosol transport is accomplished through the means of allowing larger droplets to penetrate to the flame. (5) Interference effects are significantly worse when larger droplets are allowed to reach the flame.

For ICP nebulizers some very interesting trends are observed which are quite contrary to what one might predict. In general, those nebulizers/spray chambers which allow a smaller proportion of the aerosol to reach the plasma give the best analytical performance in terms of detection limits. However, this becomes less surprising when taken in conjunction with our earlier fundamental studies of the influence of water vapor on ICP signals. What appears to be responsible for the inverse relationship between transport efficiency and detection limit is the increased water loading. This has a negative influence on the emission signal from the plasma.

5. Characterization of Ultrasonic Nebulizers for the ICP

As a further part of our studies relating to various techniques for aerosol formation, we have studied the operation of a commercially available ultrasonic nebulizer system (Plasma Therm). This is based on the system described by Olson, Fassel and Kniseley. We have been making a systematic study of the influence of system variables, such as liquid flow across the transducer face, and power density, on the aerosol properties produced by the nebulizer. We have used our standard aerosol characterization techniques to determine the influence of these variables upon drop size distribution and transport efficiency of the system. This has led us to believe that the limitation on efficiency of aerosol production with the current system results from inadequate power density in the liquid film on the surface of the transducer. We were able to obtain the highest transport efficiencies with this system working with a liquid flow of 0.3 mL a minute, and the highest available of power 50 watts. Maximum transport efficiency was approximately 40%. We are presently investigating means to improve the power density loading in the liquid film, either by modifying the liquid interaction with the transducer, or by raising the power loading in the transducer itself. By this means we hope to accomplish a more efficient operation of the transducer for the production of small aerosol particles.

Additionally, we have noticed some very interesting effects on the actual drop size distributions produced by varying the power density in the transducer. In fact, the drop size distribution appears to be bimodal. By controlling power density, it is possible to change the relative magnitudes of the two peaks in this distribution. This could be important in terms of the interaction of the aerosol with the plasma. The influence of water loading with the ultrasonic generator is also to be investigated.

Publications During Period 8/1/82-4/26/83

1. "Aerosol Transport Model for Atomic Spectrometry", Richard F. Browner, Andrew W. Boorn and David D. Smith, Anal. Chem. 1982, 54, 1411.

2. "Effects of Organic Solvents in Inductively Coupled Plasma Atomic Emission Spectrometry", Andrew W. Boorn and Richard F. Browner, Anal. Chem. 1982, 54, 1402.

3. "Response to Comments on Measurement of Aerosol Transport Efficiency in Atomic Spectrometry", Richard F. Browner and David D. Smith, Anal. Chem. 1983, 55, 373.

4. "Sample Introduction for Inductively Coupled Plasmas and Flames" (Review), Richard F. Browner, Trends in Analytical Chemistry, 1983, 2, 121.

5. "Elimination of Matrix Vaporization Interferences in Flame AAS", David D. Smith and Richard F. Browner, Anal. Chem. 1983, Submitted for publication.

6. "Influence of Drop Size on Analytical Signals in Flame AAS", David D. Smith and Richard F. Browner, Spectrochim. Acta B, 1983, Submitted for publication.

7. "Surface Tension Effects on Aerosol Properties in Atomic Spectrometry", John Farino and Richard F. Browner, Appl. Spectrosc. 1983, Submitted for publication.

8. "Flow Injection System for Analysis of μL Samples of Biological Materials", Arthur Faske and Richard F. Browner, Appl. Spectrosc., 1983, Submitted for publication.

9. "Electrothermal Vaporization for ICP Spectrometry", Stephen Long, Richard D. Snook and Richard F. Browner, Spectrochim. Acta B, 1983, Submitted for publication.

School of Chemistry
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Georgia Institute of Technology
Atlanta, Georgia 30332
A Unit of the University System of Georgia

June 4, 1985

Ms. Loretta Hensley
National Science Foundation
Division of Grants and Contracts
Award Accountability Branch
1800 G Street, N.W.
Washington, DC 20550

Dear Ms. Hensley:

FINAL REPORT ON NSF GRANT NO. CHE-8019947

I am enclosing the final project report, including Form 98A, for the above grant. Action is pending on funding for a new grant, NSF NO. CHE-8503090 which I hope will be able to proceed following receipt of this information.

Yours sincerely,

Richard F. Browner
Professor

rfb/pc

Enclosures

cc: John Schonk, OCA

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology Atlanta, GA 30332	Chemical Analysis	CHE-8019947
	4. Award Period From 8.1.81 To 1.31.85	5. Cumulative Award Amount $294,137.00

6. Project Title

Sample Preparation and Introduction for Analytical Atomic Spectroscopy

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

Fundamental studies with aerosol sample introduction to combustion flames and high temperature radiofrequency inductively-coupled plasmas have led to significant improvements in analytical performance in atomic spectrometry. Specifically, matrix interferences in atomic absorption spectrometry have been virtually eliminated, and absolute detection limits in inductively coupled plasma atomic emission spectrometry have been improved.

A key to the progress has been the continued development of accurate, reliable measurement techniques for aerosol characterization. For example, the mass transport properties of aerosols may now be readily and reliably measured. This has allowed a working predictive model of aerosol transport properties to be developed. The nature of the solvent, either aqueous or organic, in which the analyte is introduced to the inductively coupled plasma has been shown to have a profound effect on plasma excitation properties.

A unique monodisperse aerosol generator has been developed, which will allow fundamental studies to be carried out of the influence of drop size on analytical signals and interferences in atomic spectrometry. The device produces drops selectable in the range of approximately 5-100 μm by purely mechanical means, without the need for an external source of high frequency disturbance.

Studies of sample transport have also been made with microsample introduction. In one experiment, sample solution was into a flowing liquid stream, and in the other of desolvated particles generated with an electrothermal vaporizer. Both studies have provided valuable insight into the transport processes active in each case, but have pointed to the need for further work.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (√)	Approx. Date
a. Abstracts of Theses		X			
b. Publication Citations		X			
c. Data on Scientific Collaborators		X			
d. Information on Inventions		X			
e. Technical Description of Project and Results		X			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
Richard F. Browner		6.4.85

IIIa. ABSTRACTS OF THESES SUPPORTED BY GRANT

1. Marilyn S. Black, Ph.D. (1981).

A Study of Sample Introduction for Inductively Coupled Plasma Atomic Emission Spectrometry Using Volatile Metal Chelate Complexes

This research describes a new technique for inductively coupled plasma (ICP) sample introduction, in which metals are converted directly to their volatile metal β-diketonates and introduced directly into the ICP as vapor. The metals Zn, Co, Mn, Fe, Cr, Be, Al, V, Cu, and Ni, have been successfully converted and vaporized as their metal trifluoroacetylacetonates and detected by ICP-AES. Operating parameters were optimized to achieve excellent plasma stability and efficient sampler introduction. The feasibility of reacting pure metals and metals in biological materials trifluoroacetylacetone (tfa) and hexafluoroacetylyacetone (hfa) is illustrated by qualitative and quantitative data. Metals ranging in concentration from μg/g to ng/g are directly extracted from various biological materials (e.g. bovine liver, blood serum, and skin) with good recoveries (in general >90%) and acceptable precision (≥14% rsd). This chelation/ICP-AES technique requires minimal sample preparation and only mg to ng amounts of material.

Additionally, pneumatic nebulization of organic solutions of metal trifluoroacetylacetonates is discussed. Quantitative data are presented for the determination of metals in various biological matrices various extraction procedures. Multielement solvent extraction is shown to offer a selective analytical approach when pneumatic nebulization is required.

2. David D. Smith, Ph.D. (1983).

Fundamental Studies of Aerosol Sample Introduction in Optical Atomic Spectrometry

Direct procedures for carrying out aerosol transport efficiency measurements have been developed. These procedures, which involve collection of aerosol on either filter media or with a cascade impactor, have been compared with several indirect procedures. In all instances, the direct procedures have provided superior accuracy and precision to the indirect procedures. The discrepancy is particularly noticeable with low efficiency inductively coupled plasma systems, where indirect procedures can give positive errors of up to 300%.

An aerosol transport model has been developed which describes the successive steps of aerosol generation and modification by various devices used in atomic spectrometry. The development of this model has been made possible by the availability of accurate methods for measuring transport efficiency and drop size distribution developed in this research. The aerosol modifiying process is considered in three stages. The primary stage, aerosol generation, is described empirically using the Nukiyama and Tanasawa equation. The secondary stage involves interaction of the primary aerosol with an impact bead or mixer paddle. The final (tertiary) stage involves aerosol loss processes such as impaction, centrifugation, gravitational settling, and also evaporation processes. The interaction of these successive steps produces a tertiary aerosol at the atomizer with a much narrower size distribution than the primary aerosol. This results from predominant loss of larger diameter drops from the aerosol, and also ensures that the transport efficiency of typical systems is only in the range 0.5-10%.

Condensed phase interference effects in atomic absorption spectrometry have been investigated for a wide range of elements in both the air/acetylene flame and the nitrous oxide/acetylene flame. By suitable control of drop size, almost all of the interferences reported in the literature (e.g. Ca/PO_4^{3-}, Mg/Al etc.) may be eliminated.

IIIb. PUBLICATIONS SUPPORTED BY GRANT

1. "Determination of Metal Chelates by Inductively Coupled Plasma Atomic Emission Spectrometry and Applications to Biological Materials," Marilyn S. Black, Michael B. Thomas and Richard F. Browner, Anal. Chem. 53, 2224 (1981).

2. "Spray Chamber Placement and Mobile Phase Flow Rate Effects in Liquid Chromatography/Inductively Coupled Plasma Atomic Emission Spectrometry," Brenda S. Whaley, Kimberley R. Snable and Richard F. Browner, Anal. Chem. 54, 162 (1982).

3. "Measurement of Aerosol Transport Efficiency in Atomic Spectrometry," David D. Smith and Richard F. Browner, Anal. Chem. 54, 1411 (1982).

4. "Effects of Organic Solvents in Inductively Coupled Plasma Atomic Emission Spectrometry," Andrew W. Boorn and Richard F. Browner, Anal. Chem. 54, 1402 (1982).

5. "Aerosol Transport Model for Atomic Spectrometry," Richard F. Browner, Andrew W. Boorn and David D. Smith, Anal. Chem. 54, 533 (1982).

6. "Response to Comments on Measurement of Aerosol Transport Efficiency in Atomic Spectrometry," Richard F. Browner and David D. Smith, Anal. Chem. 55, 373 (1983).

7. "Sample Introduction for Inductively Coupled Plasmas and Flames," (Review), Richard F. Browner, Trends in Analytical Chemistry 2, 121 (1983).

8. "Sample Introduction: The Achilles Heel of Atomic Spectroscopy?" Richard F. Browner and Andrew W. Boorn, Anal. Chem. **56**, 786A (1984).

9. "Sample Introduction Techniques for Atomic Spectroscopy" Richard F. Browner and Andrew W. Boorn, Anal. Chem. **56**, 875A (1984).

10. "Sample Introduction for Atomic Spectroscopy: The Oldest Problem, The Newest Frontier", Richard F. Browner, Proc. Roy. Soc., Analyt. Divn., **21**, 314, (1984).

11. "Surface Tension Effects in Atomic Spectrometry", John Farino and Richard F. Browner, Anal. Chem. **56**, 2709, (1984).

12. "Influence of Aerosol Drop Size on Signals and Interferences in Flame Atomic Absorption Spectrometry", David D. Smith and Richard F. Browner, Anal. Chem. **56**, 2702, (1984).

13. "Some Observations on Electrothermal Vaporization for Sample Introduction to the Inductively Coupled Plasma," Stephen E. Long, Richard D. Snook and Richard F. Browner, Spectrochim. Acta B, **40B**, 553, (1985).

14. "Flow Injection System for Analysis of uL Samples of Biological Materials," Arthur Faske and Richard F. Browner, Appl. Spectrosc. **39**, 542, (1985).

15. "Influence of Drop Size on Analytical Signals in Flame AAS," David D. Smith and Richard F. Browner, Spectrochim. Acta B, 1984, submitted for publication.

16. "Monodisperse Aerosol Generator for Spectroscopic Applications", Ross C. Willoughby and Richard F. Browner, Rev. Sci. Instrum. 1985, submitted for publication.

IIIb. (cont.) CONFERENCE PRESENTATIONS OF MATERIAL SUPPORTED BY GRANT

1. "Sample Introduction: The Achilles Heel of Atomic Spectrometry", Richard F. Browner, University of Alberta (1981), **invited talk.**

2. "Influence of Aerosol Formation and Transport Processes on Analytical Signals and Interferences in Atomic Spectrometry", R. F. Browner, D. D. Smith and

A. W. Boorn, 9th International Conference on Atomic Spectroscopy and XXII Colloquium Spectroscopicum Internationale, Tokyo, Japan (1981).

3. "Evaporation Characteristics of Aqueous Aerosols Using Mie Laser Scattering Techniques", R. Kull, R. F. Browner, 8th Federation of Analytical Chemistry and Spectroscopy Societies Meeting (FACSS), Philadelphia (1981), **invited talk.**

4. "Correlations Between Aerosol Particle Size and Interference Effects in Atomic Spectrometry", D. D. Smith, R. F. Browner, 8th FACSS Meeting, Philadelphia, PA (1981), **invited talk.**

5. "Interactions of Organic Solvents with Low Power Ar ICP Discharges", A. W. Boorn, R. F. Browner, 8th FACSS Meeting, Philadelphia, PA (1981).

6. "Flow Injection Analysis with ICP Spectrometry", A. W. Boorn, K. R. Snable, B. S. Whaley, R. F. Browner, 6th National Conference on Spectrochemical Excitation and Analysis, Edgartown, MA (1981).

7. "Fundamental Parameters of Liquid Sample Introduction to the Inductively Coupled Plasma", Richard F. Browner, 1982 Winter Conference on Plasma Spectrochemistry, Orlando, FL (1982), **invited talk.**

8. "Sample Introduction Routes for Atomic Spectrometry", R. F. Browner, North Carolina State University (1982), **invited talk.**

9. "Atomic Spectrometry with Flames and Plasmas", Richard F. Browner, Sheffield Polytechnic (1982), **invited talk.**

10. "Flames and Plasmas - The Role of the Sample", Macaulay Institute for Soil Research, Aberdeen, Scotland (1982), **invited talk.**

11. "Aerosol Transport Model for Atomic Spectrometry", ARAAS Meeting, Sheffield, U.K. (1982), **invited talk.**

12. "Influence of Surface Tension on Drop Size Distributions in Atomic Spectrometry", J. Farino and R. F. Browner, 9th Federation of Analytical Chemistry and Spectroscopy Societies' Meeting (FACSS), Philadelphia, PA (1982), **invited talk.**

13. "Atomic Absorption Volatilization Interferences: Fact or Fiction?", David D. Smith and Richard F. Browner, 9th FACSS Meeting, Philadelphia, PA (1982), **invited talk.**

14. "Pneumatic Nebulization in Plasma Emission Spectroscopy", Andrew W. Boorn and Richard F. Browner, 9th FACSS Meeting, Philadelphia, PA (1982), **invited talk.**

15. "Influence of Water Vapor and Aerosol on ICP Emission Signals", Ray Kull and Richard F. Browner, 9th FACSS Meeting, Philadelphia, PA (1982), **invited talk.**

16. "The Role of Sample Introduction in Atomic Spectrometry", Richard F. Browner, Department of Chemistry, University of North Carolina, Chapel Hill (1982), **invited talk.**

17. "Advances Towards High Sensitivity, Sample Independent Methods in Atomic Spectrometry", Richard F. Browner, Georgia Section A.C.S. Meeting (1982), **invited talk.**

18. "Influence of Surface Tension on Drop Size Distributions in Atomic Spectrometry", J. Farino, R. F. Browner, 9th FACSS Meeting, Philadelphia, PA (1982), **invited talk.**

19. "Influence of Water Vapor and Aerosol on ICP Emission Signals", R. Kull, R. F. Browner, 9th FACSS Meeting, Philadelphia, PA (1982), **invited talk.**

20. "Pneumatic Nebulization in Plasma Emission Spectrometry", A. W. Boorn, R. F. Browner, 9th FACSS Meeting, Philadelphia, PA (1982), **invited talk.**

21. "The Role of Sample Introduction in Atomic Spectrometry", Dept. of Chemistry, University of North Carolina, Chapel Hill, Analytical Division Seminar (1982), **invited talk.**

22. "Advances Toward High Sensitivity, Sample Independent Methods in Atomic Spectrometry", Georgia Section, American Chemical Society (1982), **invited talk.**

23. "Sample Introduction for Flames and Plasmas", Villanova University, Dept. of Chemistry (1982), **invited talk.**

24. "Sample Introduction for Atomic Spectrometry", Emory University, Dept. of Chemistry (1983), **invited talk.**

25. "Optimum Aerosol Properties for ICP Sample Introduction", R. Kull, R. F. Browner, 34th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (1983).

26. "Tertiary Aerosol Characterization of ICP and AA Nebulizers and Spraychambers", J. Farino, D. D. Smith and R. F. Browner, 34th Pittsburgh Conference (1983).

27. "Flow Injection Analysis of uL Samples of Biological Materials Using ICP Detection", A. Faske, K. R. Snable, A. W. Boorn and R. F. Browner, 34th Pittsburgh Conference (1983).

28. "Influence of Particle Size on Signals and Interferences in AAS", D. D. Smith, R. F. Browner, 34th Pittsburgh Conference (1983).

29. "Sample Introduction for Flames and Plasmas - Defining Objectives", R. F. Browner, Symposium - "Atomic Spectroscopy - Where Next?", 34th Pittsburgh Conference (1983), **invited talk.**

30. "Sample Introduction in Atomic Spectrometry: The Oldest Problem, the Newest Frontier", R.F.Browner, Silver Medal Lecture, Royal Society of Chemistry, Analytical Division Meeting, University of Loughborough, U.K. (1983).

31. "Sample Introduction in Atomic Spectrometry: The Oldest Problem, the Newest Frontier", R.F. Browner, Analytical Division, Scottish Region Royal Society of Chemistry/Inorganic Chemistry Section, Strathclyde University, U.K. (1983), **invited talk.**

32. "Novel Methods of Sample Introduction for the ICP", R.F. Browner, SAS Tour Speaker: 1. Corning, N.Y., 2. Buffalo, N.Y., 3. Washington, D.C., 4. Dalhousie University, Halifax, N.S., Canada (1983), **invited talks.**

33. "Model of Sample Introduction in Atomic Spectrometry", R.F. Browner, SAS Tour Speaker: Pittsburgh, PA (1983), **invited talk.**

34. "Interference Effects in Atomic Spectroscopy from Liquid Sample Introduction", R.F. Browner, U.S. EPA Seminar on Atomic Spectroscopy, Cincinnati, OH (1983), **invited talk.**

35. "Liquid Sample Introduction for Atomic Spectroscopy: Defining the Basics", R.F. Browner, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N.J. (1984), **invited talk.**

IIIc. SCIENTIFIC COLLABORATORS

1. Eugene A. Powell, Research Engineer, School of Aerospace Engineering
2. Stephen E. Long, Postdoctoral Associate
3. Marilyn S. Black, Graduate Student
4. David D. Smith, Graduate Student
5. Ross C. Willoughby, Graduate Student
6. Ray Kull, Graduate Student
7. John Farino, Graduate Student
8. Jonathan Miller, Graduate Student
9. Arthur J. Faske, Graduate Student

IIId. INVENTIONS RESULTING FROM PROJECT

A US patent application has been filed for a monodisperse aerosol generator, based on the NSF sponsored research. The application is presently under consideration by the Patent Office.

IIIe. TECHNICAL DESCRIPTION OF PROJECT AND RESULTS

The following section describes in outline the research that has been carried out during the period of the current grant.

1. **Nebulization Transport Efficiency Measurement.** The effort previously pursued, under an earlier grant, of developing definitive techniques for characterizing of aerosol transport and transport properties in atomic spectroscopy has continued. Specifically, a major comparative study of various techniques for measurement of aerosol transport efficiency has been made. This study has shown that indirect methods can lead to estimated values of transport efficiency up to 300% high. This is a direct consequence of the simple arithmetic of indirect measurements, and the consequent need for accuracy beyond the capabilities of any normal system. It has been shown conclusively that many of the techniques described in the literature give significant positive errors. As a consequence, literature values obtained by indirect procedures must be considered suspect. Surprisingly, many authors continue to use indirect procedures for determining transport efficiency, which points to the need for continued awareness in the area. Any meaningful comparison of sample introduction systems must be based on reliable and accurate transport efficiency, or preferably analyte mass transport, measurements.

2. **Organic Solvent Sample Introduction for ICPs.** The influence of organic solvents on the inductively coupled plasma has long been something of a mystery. Certain solvents, such as xylenes, appear to be routinely simple to introduce, whereas other solvents, such as methanol, heptane etc., can actually extinguish the plasma. This highly unsatisfactory state of affairs had not been studied systematically prior to the current work.

It proved possible, through studying a wide range of solvents, to make a satisfactory correlation between the evaporation rates of the various solvents and their influence on plasma stability. The influence of particular solvents could be characterized by class, e.g. chlorinated solvents showed different properties from oxygenated solvents, or from hydrocarbons. However, within a particular group of solvents there was a clear correlation between the volatility of the solvent and its capacity to extinguish the plasma. Through this work, the generally poor

performance of organic solvents in ICP spectrometry was explained. Although volatile solvents gave rise to improved analyte transport efficiency, this improvement was often more than counterbalanced by the temperature lowering effect of the solvent on the plasma. The more volatile the solvent, the greater the solvent vapor loading in the plasma, and hence the greater the temperature lowering of the plasma. The practical solution was found to be the partial removal of solvent vapor with a condenser. This restored the signal gains which had previously been anticipated on the basis of improved analyte transport efficiency. By this means, enhancements could be obtained for most solvents with the ICP.

3. **Aerosol Transport Model for Atomic Spectrometry.** In this study, an attempt was made to develop a model for the stages of sample introduction; from nebulization, through interaction with the spraychamber, to the flame or plasma. The primary goal of this work was to show that the **overall** performance of the sample introduction system can only be properly understood by considering the interaction of each component of the system on the aerosol produced by the nebulizer. Both the mass delivery rate, and the drop size distribution of the aerosol reaching the atomizer, is determined by this interaction. This work showed the following for the first time: that in order to understand the drop size characteristics of the aerosol reaching the analytical flame or plasma (the tertiary aerosol), it was necessary to consider a two- or three-stage process, in which the aerosol with a wide size distribution which is produced at the nebulizer, (the primary aerosol), interacted with the spraychamber. The function of the spraychamber was essentially to reject large drops, according to the dominant mechanism active with that chamber. The resulting tertiary aerosol would finally pass to the flame or plasma.

The model derived in this work attempted to show how these concepts could be applied, at least semiquantitatively, to a typical AAS pneumatic nebulizer/spraychamber system. The calculations showed that certain of the mechanisms discussed were indeed appropriate to describe the process of sample introduction for the AAS system. Additionally, it proved possible to distinguish between several possible competing mechanisms for the aerosol loss process. For ICP spraychambers, a novel process of turbulent loss was postulated.

In the course of this study, many approximations, some of them quite significant, were necessary. However, for the AA nebulizer/spraychamber system, remarkably good correlation between theory and experimental data was found. Further concepts of general significance introduced in this study were: (1) a discussion of the appropriate terms to describe analyte transport to a flame or plasma, and (2) the concept of useful (W_u) and excess (W_e) aerosol, contained within the tertiary aerosol. The dividing line, d_{max}, between useful and excess aerosol, was defined as the diameter of the particle whose size is such that it contributes 10% or less to the analytical signal. This is felt to be a novel and important concept, of major importance to describing the onset of vaporization interferences in atomic spectroscopy.

This study was aimed to have the widest possible scope, in terms of general applicability to all atomic spectrometric systems. As a consequence, many areas of major importance were not studied in detail. The intention was, and is, to carry out much more careful studies at a later date, in order to derive models

applicable to other popular experimental systems.

4. Reduction of Matrix Vaporization Interferences in Flame AAS. This study is a logical extension of the work described in the previous section. The concept of a **maximum** particle size which can give rise to useful signal (d_{max}), suggests that a **reduction** in the mass of analyte reaching the atomizer contained in drops **larger** than d_{max} should reduce, or remove, vaporization interferences. Many such matrix vaporization interferences have been described in the atomic absorption literature.

A clear pointer that careful control of aerosol properties could indeed effectively remove all vaporization interferences in atomic absorption was given 16 years ago by Stupar and Dawson. This work, remarkably, had not led to further research. Our studies have shown that it is possible to virtually eliminate all residual vaporization interferences in AAS by careful control of the size distribution of the tertiary aerosol introduced to the AA flame. Furthermore, by studying the properties of some modern AA nebulizers, it was shown that some of the newer devices using impact beads **can actually give rise to vaporization interferences that had effectively already been removed by the use of earlier AA spraychambers.** This study pointed to the need for careful characterization of the aerosol properties of any new sample introduction system. Otherwise the researcher, or instrument manufacturer may unknowingly reverse the gains made in interference reduction, through single-mindedly pursuing the goal of lower detection limits. The most direct means of achieving lower detection levels, and that unfortunately used by the manufacturers, involved allowing coarser aerosol drops to reach the flame. Predictably, coarser drops result in greatly enhanced matrix vaporization interference effects.

The conclusion to be drawn from this study is that a proper understanding of the aerosol related properties of sample introduction processes is essential, in order to optimize signals, and minimize interferences in atomic spectroscopy.

5. Surface Tension Effects on Aerosol Properties in Atomic Spectrometry. The role of surface tension has never been clearly defined in studies of the fundamentals of sample introduction. In fact, the literature contains many conflicting reports regarding the role of surface tension as: (a) an enhancer, (b) a reducer, (c) a neutral on analytical signals. The aim of this study was to make a systematic attempt to determine the influence of surface tension on signals in both AAS and ICPAES. Both organic solvents and aqueous solvents containing surfactants were studied.

The results showed that the application of the aerosol transport model, described earlier, to the current case is generally an accurate one. Quite a good correlation was obtained between aerosol generation and transport properties, and the analytical signals observed. Furthermore, the study was able to show, by measuring the tertiary aerosol produced with all systems, that in fact surfactants **do not produce any significant reduction in the drop size distribution of tertiary aerosols reaching flames or plasmas.** Consequently, statements in the literature regarding the influence of surfactants on drop size are apparently in error. There was shown to be a fundamental difference in surface tension forces active with **organic solvents** compared to those active with **surfactants added to aqueous solutions.** The organic solvents indeed showed a decrease in mean droplet size, as

a consequence of reduced surface tension, compared to aqueous solvents. Aqueous solvents containing surfactants, and having comparable surface tension to the organic solvents, showed no decrease in mean tertiary drop size. It was hypothesized that this difference is due to the different mode of action of the surface tension forces in the two different systems. With organic solvents, the surface tension is essentially the consequence of a bulk property of the liquid, whereas the addition of surfactants requires the orientation of molecules in the liquid surface. The process of aerosol formation, which probably occurs in a matter of fractional microseconds, is too rapid to allow re-orientation of surfactant molecules in the newly created surface, and the establishment of an equilibrium surface tension value does not occur.

6. **LC/ICP and FI/ICP Interfacing Studies.** The primary weakness of interfacing LC and FI systems to ICPs lies in the poor (typically 0.5-2%) transport efficiency of the interface. This situation can be improved somewhat by the direct introduction of micro LC effluent through an in situ nebulizer placed in the plasma torch. However, this approach does not totally address the need for the significant signal enhancement with interference freedom that is called for.

We have carried out some detailed studies on the operation of LC/ICP interfaces. These showed how existing systems may be optimized, and pointed out some important parameters to be considered: (1) Placement of the spraychamber external to the plasma box reduces analyte dispersion, and improves peak height and reproducibility substantially (2) with this arrangement, peak height is largely insensitive to LC flow rate. This is a very important factor when chromatographic performance must be optimized independently.

The design of a very simple flow injection system has been described. This allows accurate data to be obtained from samples with total volumes down to and below 50 μL. The system has been shown to provide good accuracy for the analysis of biological matrices, such as NBS SRM bovine liver and synthetic Fe and Co enzyme systems.

7. **Solvent Sensitivity of ICP Emission Lines.** In many studies of system optimization with ICPs, the sample introduction system has been taken as a constant factor. That this is an unwarranted assumption has been pointed out in many of our publications, and confirmed in a recent study with miniature ICP torches.

A typical total water loading for an ICP, with pneumatic nebulization, is approximately 20 mg/min at 298 K. In the experiments carried out, additional water and aerosol could be added to the gas stream, up to about 40.4 mg/min. The rest of the system (e.g. plasma, gas flows etc.) was completely unchanged. Over the water range considered, signals from the Na(I) 589.6 nm and Mg(I) 285.21 nm lines experienced roughly a 40% drop, the signal from the Mg(II) 279.6 nm line showed a 90% drop, and the signal from the Mn(II) 257.61 nm line, with the highest combined ionization and excitation potential, **showed a drop of 97%.** This high sensitivity of line emission intensity to water vapor loading indicates dramatically the relevance of water loading to ICP emission signals. It might seem remarkable, in view of these dramatic trends, that studies of this type have not been published previously. We contend that this is merely symptomatic of the lack of concern for

fundamental studies of sample introduction from which atomic spectroscopy has suffered for so long.

Water loading is of course a function of both nebulizer design and spraychamber operation. However, additionally, it is also a critical function of system temperature. Our studies have indicated that the nebulizer argon is saturated, or slightly supersaturated, with solvent vapor. Hence the vapor loading in the plasma, and consequently the analytical signal, is highly sensitive to operating system temperature. In order to compare response of different emission lines to water loading, we define a water loading sensitivity, S_w, in the following way:

$$S_w = 100\ (\Delta I/I)\ /\ \Delta\,\mathrm{Wat} \qquad (1)$$

where ΔI is the difference in signal intensity for the two water loadings, I is the signal for the reference water loading, and ΔWat is the change in water loading (mg/min).

The S_w values shown in Table 1 indicate that for atom lines of low excitation potential the greatest sensitivity is found for water vapor, and water aerosol produces little effect. Much higher sensitivity is seen with changes in water aerosol for lines with higher total ionization and excitation potential, such as Mg (II) and Mn (II).

Table 1. Water Loading Sensitivity

Line	Water Vapor	Water Aerosol
Na(I) 588.99	1.2	0
Mg(I) 285.21	1.8	7.6
Mg(II) 279.55	3.5	25.6
Mn(II) 257.61	4.6	22.5

In some situations, there may be a significant **reduction** in water loading to the plasma, below the reference level of 20 mg/min used here. This would occur with the introduction of wholly or partially desolvated aerosols to the plasma. In this situation, the trends are somewhat different. For example, in the case of the Mg(I) 285.21 nanometer line, approximately halving the solvent loading to 13 mg/min produces roughly a doubling in signal.

Dry vs. Wet Aerosol

When the aerosol introduced to the ICP is largely desolvated ("dry"), and then enough water vapor or aerosol is added to the sample injection gas stream to return the plasma water loading to its original level, there is a dramatic difference in behavior from that found with "wet" aerosols. There is found to be essentially no water loading sensitivity for the Mg(I) 285.2 nm line.

This has important implications for the mechanisms of analyte vaporization in the plasma in the two (dry and wet) modes of introduction. It would appear that the localized environment of the evaporating particle in the plasma is of major importance in determining the excitation properties of that element in the plasma. When the particle containing analyte is surrounded intimately by solvent vapor from the evaporating solution containing the analyte, there is clearly substantial sensitivity to water loading. When, on the other hand, the particle is already pre-dried, this sensitivity appears to be absent.

Additional data was obtained with commercially available systems. In these studies, the configuration of the spraychamber was changed in order to allow different masses of analyte and solvent to arrive at the plasma per second. In essence, then, the experiment consisted of taking a single nebulizer, and operating it with three different spraychamber configurations.

The open system gave the coarsest aerosol, also fractionally the highest analyte mass delivery rate of analyte. The spraychamber designated B gave an essentially similar drop size distribution. Transport through the Scott chamber gave slightly higher analyte mass transport to the plasma, but gave the greatest water delivery rate. No significant differences in electron density or excitation temperature were found over the range of viewing heights from 0 to 30 mm above the plasma. The data in Table 2 show the danger of assuming that background is a constant percentage of noise for different sample introduction systems. What is clear from the table is that the GMK system, with has the lowest signal-to-background ratio for Ca emission actually has the best detection limit. The signal-to-noise ratio is 4.7x higher than for the B system, whereas the signal-to-background ratio is 4.8x poorer than for the B system. By contrast, for copper the Open system has the lowest signal-to-background ratio, but the second lowest signal-to-noise ratio.

Table 2. Emission Behavior of Several Nebulizers and Spraychambers

System	Cu (324.7 nm)		Ca (422.7 nm)	
	S/B	S/N	S/B	S/N
GMK	7	895	1.7	1013
2B	17	1230	8.1	215
Open	12	1050	5.1	338

In this practical situation it is clearly very difficult to deconvolute the relative influences and importance of drop size, solvent vapor loading and aerosol loading on plasma properties. Although it is clear from bulk measurement of the plasma that the **net** effect on the plasma from the point of view of excitation temperature, and electron densities is negligible. Clearly what is of importance here is the **microscopic** behavior of the solvated drops and the desolvating particles in the plasma in the expanding environment of solvent vapor. It is clear that this situation must be addressed if any true comprehension of plasma properties is to be

obtained. It seems clear, also, that generalized bulk measurements, as usually carried out, will have little relevance to the sample introduction process.

8. **Development of a Monodisperse Aerosol Generator (MAG).** This device has been developed partially for atomic spectrometry and partially for liquid chromatography applications. The desolvation interface has been developed, to the present moment, explicitly for liquid chromatography/mass spectrometry interfacing. In a later part of this proposal the potential application of the complete device to atomic spectrometry will be described.

The theoretical side of monodisperse aerosol generation is, considering the maturity of the original theoretical description by Rayleigh in 1893, surprisingly still a matter of discussion and debate. Even quite recent studies suggest that the production of monosized droplets cannot occur without the action of some external disturbance on the liquid orifice. However, these studies considered millimeter-sized drops, compared to our micrometer-sized drops. We believe that the scale of the interaction is critically important in determining the dominant mechanisms.

The application of simple Rayleigh theory, based on kinetic energy versus potential energy balance, suggests that the natural production of monosized droplets is theoretically possible. We have developed a monodisperse aerosol generator (MAG)[1] using this theory which is extremely simple, robust, and effective. Whatever the specifics of the generation mechanism, the device produces a dense, essentially monodisperse aerosol which is both highly directional and highly laminar. This should be contrasted with the highly turbulent, highly polydispersed aerosol typically produced by pneumatic nebulizers. The uniqueness of the device follows from the fact that no external disturbances in the form of ultrasonic or acoustic waves are applied by any electronic device to the aerosol generator.

The liquid jet results from application of appropriate pressure, typically 300 psi, to liquid flowing into a small rigid orifice, in this case a glass capillary drawn and ground back to approximately 10 μm orifice size. Orifices can be readily fabricated in the range of 5-50 μm. Liquid emerging from the orifice forms a jet which becomes unstable and breaks into a droplet stream of very closely spaced particles. The application of a dispersing gas jet some millimeters above the tip of the glass orifice causes these droplets to be separated spatially, and consequently not to agglomerate, which they would otherwise rapidly do. By this means the inherently monosized droplets can be maintained in this form, as a dense but uniformly sized cloud of aerosol particles.

We believe that the MAG will be of considerable value in the investigation of fundamental flame and plasma properties. Possible applications of this device, and its characterization, will be presented in the section describing proposed research. An important point to note with this device is its essential difference from the Hieftje-type isolated droplet generator. The Hieftje-type device produces a highly uniform stream of droplets, one behind the other, which are spatially and

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temporally distinct from one another. With the Hieftje-type device, each droplet enters the flame at a known position, and at a known time relative to the other drops, and its properties may be individually monitored in the flame.a However, it is not readily possible with such a device, because of the rather large particles that it produces, to introduce these droplets through the normal sample introduction system (i.e. spraychamber) for flames or plasmas. The MAG produces a dense aerosol stream, as with conventional pneumatic nebulizers, but allows the aerosol to be introduced in precisely the normal manner for liquid aerosol introduction to flames or plasmas. However, now the drop size may be controlled. Additionally, as will be described later, the device readily lends itself to nearly complete aerosol desolvation. While the MAG has relatively little application to atomic absorption spectrometry, it has very great potential for inductively coupled plasma spectrometry.

9. **Fundamental Studies with Electrothermal Vaporizer Sample Introduction to the ICP.** We have made an extensive study of the analytical potential of electrothermal vaporization (ETV) for microsample introduction to the ICP. In most instances, detection limits with ETV/ICP were found to be greatly superior to those possible with direct nebulization. Detection limits were, however, generally poorer than those found with HGA/AAS. A model has been produced which describes the sample introduction process in terms of aerosol transport phenomena, in a similar manner to our aerosol transport model for liquid sample introduction. Additionally, the major interference problems, and the influence of sample properties on plasma excitation conditions (e.g. electron temperatures, electron densities, and excitation temperatures) were determined.